

Supporting information

Plasma-assisted Highly Efficient Synthesis of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ Cathode Materials with Superior Performance for Li-ion Batteries

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1. Experimental details.

The metal precursors of NiO, MnO₂ and Co₃O₄ with a stoichiometric molar ratio (Ni:Co:Mn) of 1:1:1 and lithium carbonate as a lithium source were utilized to prepare $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$. The above starting materials mixed with de-ionized water were ball-milled for 2 h followed by being dried in an oven. The as-obtained materials were introduced into the plasma-assisted tube furnace. Plasma was generated by an RF power supply at 13.56 MHz and 300 W. The synthetic temperature of the tube furnace was set at 600 °C. The flow rate of oxygen flowing through the furnace is set at 5 sccm and the total pressure in the chamber was kept at 76 Pa. The reaction time was adjusted from 20 mins to 60 mins. The layered $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ synthesized by the above process for different time is referred as PLA-LNCM-20, PLA-LNCM-40, and PLA-LNCM-60, respectively. For comparison, the conventional annealing method was also utilized to prepare $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ for different time (60 mins, 2 h and 24 h).

X-ray diffraction studies are carried using on an X-ray diffractometer (D/MAX-2200V, Rigaku, Japan) with Cu-K α radiation. SEM characterizations are applied to observe morphologies of the samples by scanning electron microscopy (Hitach S-4800, Japan).

The different $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ electrodes as fabricated above are integrated into two-electrode

CR2032-type coin cells for electrochemical measurements (RSC Adv., 2013, 3, 12088-12090.). The cells are tested within the potential range of 3.0~4.5 V using a LAND CT2001A battery tester (Wuhan, China) at room temperature. The electrochemical behaviors of $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ are studied by cyclic voltammetry on AUT85794 (made in the Netherland) with scan rate of $0.1 \text{ mV}\cdot\text{s}^{-1}$. The electrochemical impedance spectroscopy (EIS) is measured on AUT85794 with the frequency range from 100 kHz and 10 mHz.

2. Supporting Results

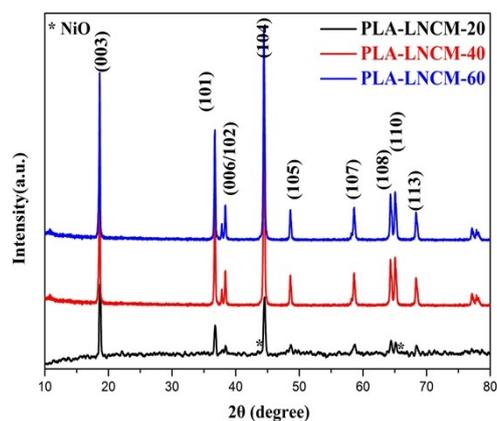


Fig. S1. XRD patterns of powders from different plasma times

Fig. S1 shows the X-ray diffraction (XRD) patterns of PLA-LNCM-20, PLA-LNCM-40, and PLA-LNCM-60. In the XRD patterns of PLA-LNCM-20, the main peaks were attributed to the layered type structure of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, while little NiO signals were also detected indicating that longer time (40 mins) is necessary to make the reaction occur completely.

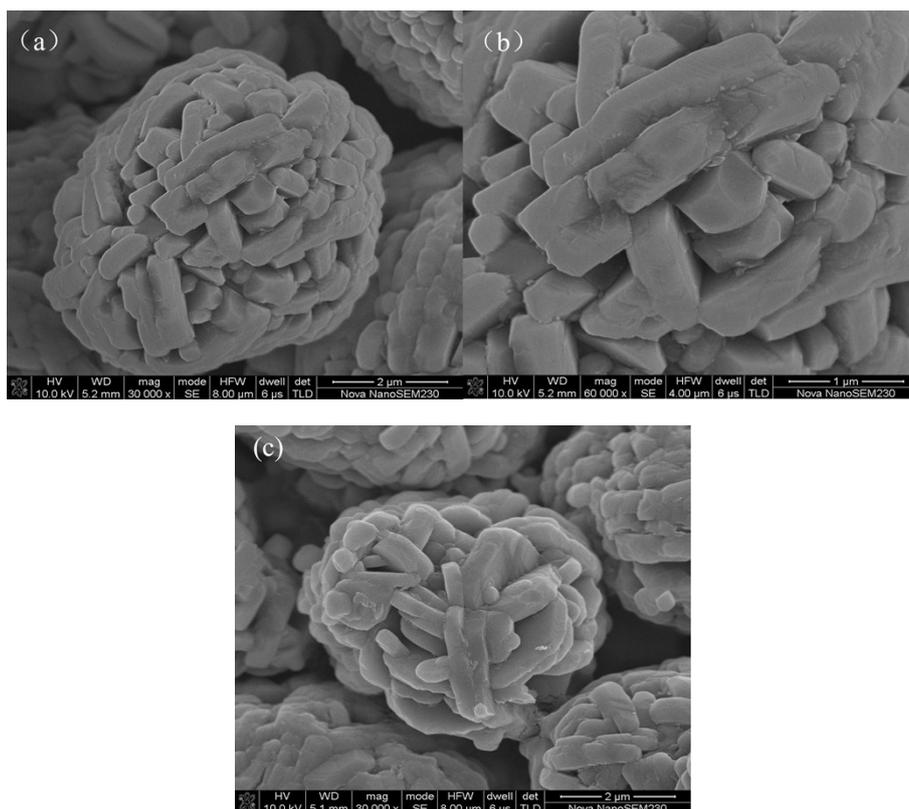


Fig. S2. a, b) SEM images of PLA-LNCM-40. Scale bars: 2 μm (a), 1 μm (b); (c) SEM image of LNCM-24h. Scale bar: 2 μm .

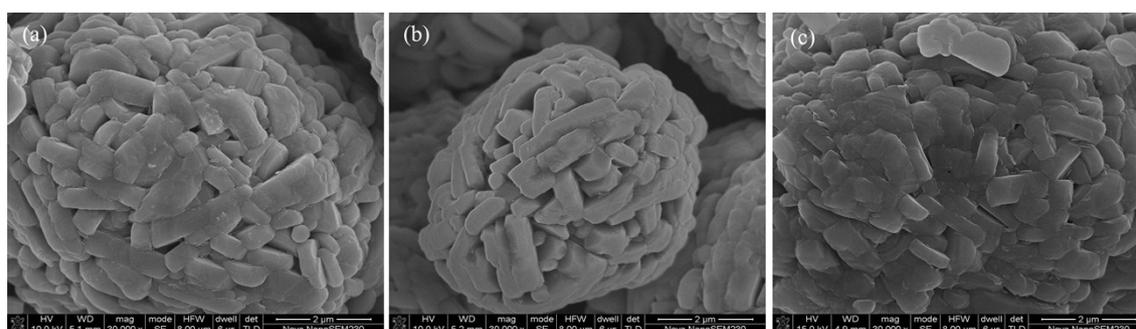


Fig. S3. SEM images of (a) PLA-LNCM-20, (b) PLA-LNCM-40, (c) PLA-LNCM-60

Fig. S3 showed particle morphologies of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized for different plasma times. Lots of small long polyhedral particles were received, which indicated the shape of the layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ in Fig. S3. Although this product of the sample PLA-LNCM-20 had

much smaller particle size ranges from 0.9 to 1.2 μm , some quasi-spherical particles could also be observed in Fig. S3a. The PLA-LNCM-40 has uniform layered morphology with the particle size ranging from 1.2 to 1.6 μm . It illustrated that the appropriate plasma time could impede the aggregation of the particles. With prolonged plasma time, the size of Fig.S3c was a little bigger than the size of Fig. S3b.

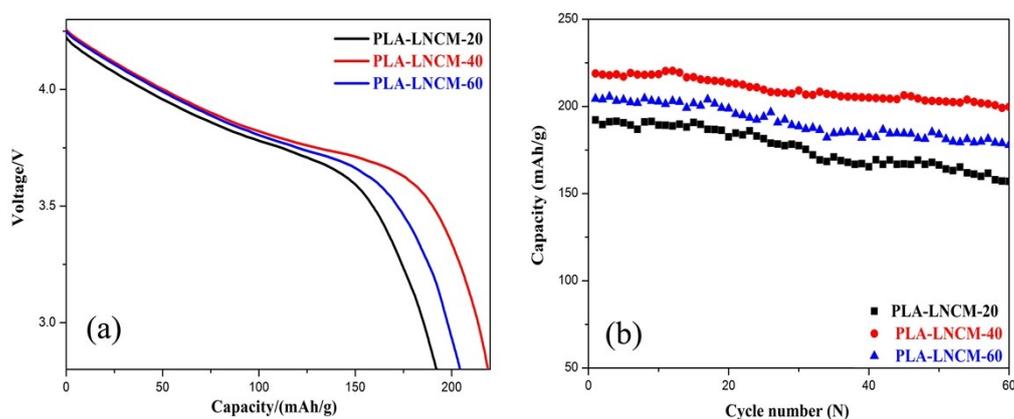


Fig. S4 Electrochemical performance of the samples with different plasma treatment times:

(a) Initial charge-discharge curves; (b) Cycling performance

In order to further study the influence of the plasma time on the electrochemical performance of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$, the tests cells were operated at the 0.1 C rate between 2.8 V and 4.3 V versus Li at room temperature. Fig. S4a showed the initial discharge curves of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ from different plasma times. The initial charge-discharge of PLA-LNCM-20 and PLA-LNCM-60 are $192.2 \text{ mAh}\cdot\text{g}^{-1}$ and $204.4 \text{ mAh}\cdot\text{g}^{-1}$. However when the plasma time was 40 min, the initial discharge capacity of $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ was $218.9 \text{ mAh}\cdot\text{g}^{-1}$. In addition, the coulombic efficiency of the three samples are 98.11%, 99.94% and 98.89% of their first charge capacities, respectively, which further illustrates the sample synthesized under the 20 min plasma time has the best electrochemical performance. At the same time, coulombic efficiency of the three samples are higher than that of that of sample LNCM-24h, which indicates the novel plasma-assisted low-temperature solid-state method is an efficient method to

synthesized cathode material. Figure S4b showed the cycling performance of the $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ synthesized from different plasma times. The capacity values for the sample PLA-LNCM-40 remained stable up to 60 cycles, which indicates it had excellent capacity-retention without noticeable capacity-fade, maintaining 91.27% of its initial capacity. The excellent cycling capability of PLA-LNCM-40 could be related to the absence of impurity (NiO) as well as the smaller particle size with a larger specific surface area.

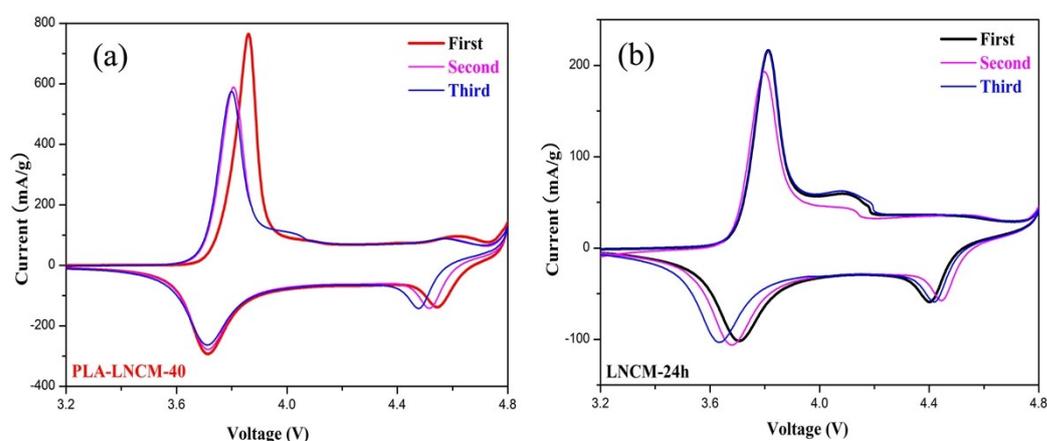


Fig.S5 CV curves of samples PLA-LNCM-40 and LNCM-24h cells collected for the first three cycles at room temperature at a scanning rate of 0.1 mV/s.

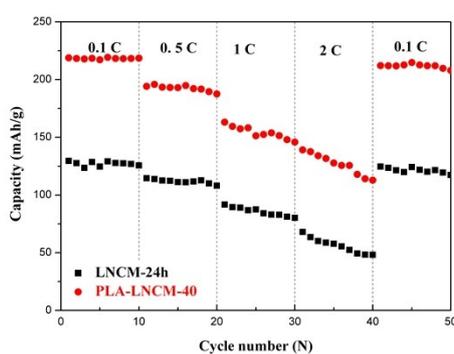


Fig. S6. Variation of discharge capacity versus cycle number for PLA-LNCM-40 and LNCM-24h electrodes cycled at 0.1, 0.5, 1, 2, 0.1 C rates between voltage limit of 2.8 and 4.3 V.

Table S1. Representative electrochemical performance for layered $\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$ from literatures.

Method	Optimal Reaction Temperature and time	Initial Discharge ($\text{mAh}\cdot\text{g}^{-1}$) (at 0.1 C)	Cut off condition (V)	Capacity retention (%)	Refs
Plasma-assisted low-temperature solid-state method	600 °C 40 min	218.9	2.8-4.3	91.27	This work
Glycine–Nitrate Combustion	1300–1400 °C * h 800 °C 4 h	138.5 (at 0.055 $\text{mA}\cdot\text{cm}^{-2}$)	2.5 – 4.3	About 93.86 (20 cycles)	5
The molten salt synthesis method	900 °C 4 h, 120 °C 12 h	164.9	3.0 - 4.4	88	6
the spray dry method	300 °C * h 900 °C 20 h	195	3.0 - 4.5	*	7
mixed hydroxide method	180 °C 12 h, 480 °C 4 h, 1000 °C 12 h	165 (at 0.19 C)	2.5 - 4.4	89.37 (40 cycles)	8
a one-pot method using the molten-salt mixture	950 °C 8 h 150 °C 24 h	150	2.5 - 4.5	About 92.66 (50 cycles)	9
the precursors derived from spray-drying method	300 °C * h 900 °C 20 h	195.3	3.0 - 4.5	81.8	10
a sol–gel method	80 °C 10 h, 120 °C 24 h, 450 °C 5 h, 900 15 h	190.8	2.5 - 4.6	74.5	11
a solvent evaporation method	100 °C * h 120 °C 12h 500 °C 6h 900 °C 20h	168.5	3 - 4.3	94.3 (30 cycles)	12
solid-state reaction method	650 °C 1 h, 950 °C 10 h	160 *	2.5 - 4.3	*	13
spray-microwave method	milled 20 h, 900 °C 2 h, Ball-milled 4h, 400 °C * h Microwave 0.5 h	140	2.5-4.3	*	14

*not mentioned

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